RAW MATERIALS

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PROMISING TECHNOLOGIES FOR REFINING CERAMIC RAW MATERIALS

A. V. Kornilov,[1] E. N. Permyakov,[1] T. Z. Lygina,[1] and Sh. Kh. Khaidarov[1]

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It is recommended that efficient refining equipment (Kaskad setup, pulsating setup, electric mass classification apparatus) be used and local unconventional types of raw materials (zeolite- and calcite-containing rock) be drawn into production to obtain from low-grade clays a wide assortment of competitive ceramic wall materials.

An important operation in the production of high-quality competitive ceramic wall building materials is preparation (refining) of clay raw materials. This technological operation plays a much larger role when the raw materials are of low grade. New and improved effective refining equipment makes it possible to draw unconditioned raw materials into the production process and to obtain highly liquid production.

The quality of clay raw materials improves when they are refined in an electric mass classifier. When mechanical activation occurs in this apparatus, the clay raw material is dispersed under "contained" impact conditions, changing the technological properties of the material to the maximum degree possible. The milling process is accompanied by changes of the granulometric as well as phase composition of the raw material. The raw material passes through stages where the naturally occurring agglomerates are destroyed and grains become partially amorphized with defects, whose energy makes possible subsequent formation of new aggregated particles which form inside them. The effect of the dispersity of the raw material during mechanical activation is not large enough for regulating the technological properties of the material. The latter are improved as a result of grain amorphization, accumulation of structural defects, and formation of heteromineral conglomerates. The degree of stability and the number of the latter are factors which qualitatively change the technological properties of polymineral clay raw materials.

As a result of the mechanical action, the initial clay material undergoes the following changes: stable state → dispersal → change of the specific surface area → appearance of structural defects (in the components of the polymineral structure) → epitaxial growth and nucleation of new phases → new stable state.

The method of activation and improving the qualitative characteristics of a material in an electric mass classifier is based on using the electrophysical and inertial properties of the particles. The raw material is refined in dry form (the moisture does not exceed 7%) in a closed vacuum. An electric mass classifier permits obtaining finely and ultradisperse uniform powder materials with particles ranging in size from 0.1 to 500 μm. The required properties of a ceramic mix are achieved by separate or simultaneous processing and enrichment of the components of the mix by changing their feed rates into the activation chamber as well as the granulometric composition of the products obtained [1].

The activation efficiency in an electric mass classifier depends on the properties of the initial clay raw material, specifically, on the sinterability. Refining of the raw material with quite high sinterability essentially does not improve the characteristics of the ceramic samples. Mechanical activation of low-quality raw material increases the compression strength of the samples by 75% and the average density by 0.07 g/cm^3. This is because clay becomes enriched as a result of comminution and fractionation and most of the clay component is found in the finely disperse fraction, which is used to form samples. In addition, structural changes also occur in the clay component, which likewise improves the quality of the raw material.

Refining low-quality clay raw material on the Kaskad-1 stand (developed by INTA-STROI JSC, Omsk) is quite effective. This stand can replace the standard refining equip-

[1] Federal State Unified Enterprise "Central Scientific – Research Institute of the Geology of Nonmetalliferous Ores," Kazan, Russia.

ment — clay grinding machine and edge-runner mill. The principle of operation of the setup consists of two actions performed on the clay: shearing cuttings from one grid and extruding through openings in another grid. In addition, the same knife is used to perform both operations. In the present laboratory setup, three rotating knives and three stationary grids are placed on the same shaft.

The investigations of low-quality raw material from deposits located in the Republic of Tatarstan have shown that refinement on the Kaskad-1 stand improves the molding properties and increases the strength of ceramic articles. Refinement essentially does not change the properties of natural raw material with sufficiently high quality.

The pulsation method of enrichment can be used to increase the quality of low-grade clay raw materials. In this case, clay particles are relatively quickly rubbed off granular material, and several clay fractions for subsequent adjustment of slip consistency are obtained. An advantage of this method is that the energy consumption is low and different reagents can be introduced into the suspension (alkali, electrochemically activated water, and others). A concentrator makes it possible to thicken clay suspensions and quickly separate and recirculate most of the water [2].

Investigations of refining on a pulsation laboratory setup were performed on clay from the Kalininskoe deposit (Tatarstan), which is a commonly occurring type of clay. Its content of a montmorillonite component lies in the range 30 – 34%.[2] The dried clay mass was comminuted to the smallest possible particle size, mixed with water in a 1 : 1 ratio, and loaded into the top entrance opening in the first section of the apparatus. During the flow along the inner receiving pipe through five screening plates, arranged uniformly along the height of the pipe, the clay is washed with fresh water introduced from below by means of air pulses. The air pulses, whose repetition period is 7 sec and duration is 2 sec, cause the suspension to oscillate with amplitude 16 – 18 cm.

As a result of refinement in the pulsation apparatus, the initial clay was actually separated into three types of fractions (with different content of the montmorillonite component — MC). The first fraction contained mainly the largest particles (> 0.063 mm), and the clay mass corresponded to a type of clay with low MC content (19 – 25%) and with hydromica predominating. Appreciably less MC (24 – 29%) was also observed in the second fraction. The third and fourth fractions were found to be close with respect to the MC content (30 – 34%) and dispersity. Most of the clay (62%) was found in the finest (fourth) fraction.

The clay was first processed with alkaline water in order to separate particles of different size into fractions more accurately and disperse the clay more quickly. In addition, water was removed from the clay mass in the third fraction by means of electro-osmosis. In this case, the highest MC was observed in the third fraction; the dispersity of the clay particles increased by an especially large amount, which can be judged by the almost doubling of the clayiness as compared with the initial clay. Ceramic obtained on the basis of the third fraction of activated (electrochemically worked and electro-osmotically dehydrated) clay exhibits the highest sintering and, correspondingly, the greatest strength. The predicted grade of semi-dry-pressed brick obtained from such press powder is at least 200 – 300. At the same time, the articles also acquire better coloring; the colors are more uniform and saturated.

[2] Here and below — content by weight.

TABLE 1.

Sample	Mix composition, %				$CaCO_3$ content, %, in lime-containing clay
	lime-containing clay	refractory clay	chamotte	quartz sand	
1	100	–	–	–	22.8
2	100	–	–	–	19.4
3	100	–	–	–	13.8
4	90	5	5	–	24.5
5	70 15	10	5	–	37.8
6	90	–	–	10	33.4

A stronger effect from the pulsation method of refinement can be expected for clays with low MC content (10 – 25%).

To expand the mineral – raw materials base and the list of ceramic building materials local unconventional types of raw material, for example, zeolite-containing silicon rock as well as zeolite- and line-containing clays, must be drawn into production [3].

It has been determined that zeolite-containing silicon rock (ZCSR) from the Tatarsko-Shatrashanskoe deposit is an effective additive to the initial mix for obtaining ceramic wall materials. Together with this additive, consumable additives (sawdust, peat) and additives which improve the sinterability of the initial materials (zeolite-containing and refractory clays) are used to change the physical – mechanical properties.

The optimal quantity of ZCSR additive is 40 – 45% depending on the amount of clay. In low-quality clay raw materials, 30% zeolite-containing clay must be added together with ZCSR (20%) to obtain a positive result. The samples formed from such mixes show compression strength 20.2 – 27.5 MPa, bending strength 4.3 – 7.0 MPa, and density 1.45 – 1.60 g/cm^3. Adding 45 – 50% ZCSR into polymineral clay raw materials makes it possible to obtain not only strong but also highly porous (with low average density) ceramic material, possessing improved heat-insulation properties.

Adding zeolite-containing clay from the Kushkuvaiskoe manifestation (Tatarstan) to polymineral clay raw material improves its sinterability. Depending on the amount added the compression strength increased by 7 – 85%. In addition, and this is very important, the density decreases by 0.06 – 0.11 g/cm^3.

TABLE 2.

Sample	Density, kg/m^3	Water absorption, %	Total shrinkage, %	Strength, MPa		Freeze resistance index	Brick index	Color
				under compression	under bending			
1	1460	24.9	4.8	12.9	2.0	F35	125	Light yellow
2	1540	21.2	4.8	16.1	2.4	F35	150	Light cream
3	1565	18.3	4.0	23.9	3.2	F35	200	Rose
4	1460	23.2	2.8	13.4	1.9	F35	100	Yellowish-light grey
5	1550	23.7	2.1	12.3	1.8	F25	100	Light yellow with a rose hue
6	1505	21.0	2.4	22.5	1.7	F25	100	Yellowish-grey

Zeolite-containing clay is not only a flux but it is also acts as a plasticizer (plasticity number 29.7 – 34.1). Introducing 10% preserves the plasticity number of the clay pastes, containing 40% ZCSR, at the level of the initial clay raw material.

Introducing ZCSR and zeolite-containing clay into clay raw materials somewhat improves its drying properties, which are directly related with the shrinkage of the samples. Thus, the coefficient of sensitivity to drying as determined by the Chizhskii method, increases from 64 – 78 to 82 – 97 sec.

Experimental batches of ceramic brick with grade 100 and higher were obtained from initial mixes (Table 1) containing polymineral low-melting clay and zeolite-containing raw materials.

Interesting results were obtained by using zeolite-containing clay together with ZCSR. For the ratio 75 : 25 of these materials, the samples have high compression strength (22.3 MPa) with low density (1.46 g/cm^3). Laboratory samples formed from mix containing 25 and 50% zeolite-containing clay have an even lower density (1.11 – 1.24 g/cm^3). Articles with such characteristics can be recommended as heat-insulating construction materials for interior work.

Batches of hollow (hollowness 11%) brick have been obtained by the semi-dry pressing method with lime-containing clays from the Maksimovskoe and Zhukovskoe deposits (Tatarstan). The pressing pressure is 24 MPa and the calcination temperature is 1050°C.

Practically all articles satisfy the requirements of the normative-technical documents with respect to the physical and mechanical properties (Table 2). Depending on the content of $CaCO_3$ in the clay initial material, the strength index varies from 100 to 200, and the color varies from rose to light yellow. Brick with similar properties can also be obtained from raw material with a higher $CaCO_3$ content (> 40%). In this case, clay raw material with the lowest possible amount of calcium carbonate (the total $CaCO_3$ content in the charge should not exceed 28%) must be added to the mix. To obtain high-quality articles the mix must be prepared more carefully with the clay placed in molds to age before it enters the production cycle and the dynamics of furnace heating must be worked out.

Adding a small quantity (about 20%) of lime-containing clay to red-firing clay imparts a novel color to brick. White point-like inclusions up to 2.5 mm in size are uniformly distributed against a light-red background.

The technological regulations for the production of light-colored ceramic brick from lime-containing clays are essentially identical to the regulations for producing articles from polymineral clays. The equipment set is the same; only the parameters of the technological process take on different values.

In summary, the production of a long list of competitive ceramic wall materials can be accomplished by using effective refining equipment (Kaskad setup, pulsation setup, electric mass classifier) and bringing zeolite- and calcite-containing rocks into the production process.

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